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The Stark effect of some supermultiplets in the arc spectrum of silicon

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With 3 figures in the text

Summary

The influence of electric fields on the Si I terms $(^2P)\,5p$ and $(^2P)\,5f$ has been measured. At the field strength 100 kV/cm the displacements of the $5p$ levels range from 0 to 4 cm^{-1}. The displacements of the $5f$ levels at 60 kV/cm range from 10 to 20 cm^{-1}. The $5p\ ^3P$ levels show an interesting case of perturbation, due to the influence of the $4d\ ^3F$ levels. The Stark effect theory for Russell-Saunders' supermultiplets is discussed and applied to the perturbations of the Si I polyads $(^2P)\ 5p\ ^1S\,^1P\,^1D$, $(^2P)\ 5p\ ^3S\,^3P\,^3D$.

1. Experimental

In the modified Lo SURDO discharge tube used in a Stark effect investigation of the arc spectrum of fluorine[1] free fluorine from decomposed SF_6 probably reacted with SiO_2 of the quartz tube to form SiF_4 which was excited in the glow discharge. Si I lines were obtained with moderate intensity, influenced to various degrees by the electric field, and also several strong Si II lines appeared. The maximum shifts of the Si I lines were measured in the same way as previously described.[1] In a few cases the difference between the field-free part and the maximum shifted part of a line was directly measured in relation to a nearby standard line, using a Cambridge Universal Measuring Machine with rectangular co-ordinates. The displacements were obtained by comparison with C. C. Kiess' wave-lengths and term values of the Si I spectrum.[2] The results of the measurements are given in Tab. 2.

2. Discussion

If an electron is added to the parent term, Si II $3s^2\ 3p\ ^2P$, a polyad arises. The calculation of the matrix element Z^{α}_{β}, i. e. the z-component of the electric dipole moment, connecting two states α and β of *polyads* is somewhat different from the calculation of Z^{α}_{β} for ordinary multiplet levels. If L_{I} is the azimuthal quantum number of the ion, l that of the added electron and L that of the whole system, a factor $f(L_{\mathrm{I}}\, l\, L)$ must be added as stated by MINNHAGEN[1], who subsequently studied these relations more thoroughly.[2] He gives general explicite formulae for Z^{α}_{β} for all definite coupling schemes. In the mean time the present author derived without rigid proof expressions for $f(L_{\mathrm{I}}\, l\, L)$ in LS-coupling based on CONDON and SHORTLEY's[3] treatment of vector coupling. They are in agreement with those cited above.[2] In the case

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[1] K. LIDÉN, Ark. Mat. Astr. Fys., *35*, no. 23, 1948.

[2] C. C. KIESS, J. Res. Nat. Bur. Stand. *21*, 185, 1938.

$$\Delta L = -1,\ \Delta J = +1,\ \Delta l = +1,\ \alpha = (L_{\mathrm{I}}, l, n, L, S, J, M),$$
$$\beta = (L_{\mathrm{I}}, l+1, n^1, L-1, S, J+1, M)$$

the following expression for Z^{α}_{β} was obtained:

$$(Z^{\alpha}_{\beta})^2 = [(J+1)^2 - M^2]\cdot\frac{(S+L-J)(J+S-L+1)(S+L-J-1)(J+S-L+2)}{4(J+1)^2(2J+1)(2J+3)}\cdot$$
$$\frac{(L_{\mathrm{I}}+l-L+1)(L+L_{\mathrm{I}}-l)(L_{\mathrm{I}}+l-L+2)(L+L_{\mathrm{I}}-l-1)}{4L^2(2L-1)(2L+1)}\cdot\frac{e^2}{4(l+1)^2-1}\cdot(R^{\alpha}_{\beta})^2.$$

The radial part R^{α}_{β} depends on the coupling between L and S. For the approximate calculations of the absolute shifts R^{α}_{β} may be computed from hydrogenic eigenfunctions for term values of comparable magnitude. The factor $f(L_{\mathrm{I}}\, l\, L)$ decreases the angular part of Z^{α}_{β}. For the actual case, viz. the polyads $(^2P)\ 5p\ {}^3S\,{}^3P\,{}^3D$, $(^2P)\ 5p\ {}^1S\,{}^1P\,{}^1D$ of Si I, the values $f(L_{\mathrm{I}}\, l\, L)\cdot\frac{1}{4l^2-1}$ are given in Tab. 1.

Table 1

The factor $f(L_{\mathrm{I}}\, l\, L)\cdot\frac{1}{4l^2-1}$ of the angular part of the matrix element of the dipole moment.

Perturbed terms	Perturbing terms			
	n s P	n d P	n d D	n d F
n p S	1/9	2/9	—	—
n p P	1/6	1/12	1/20	—
n p D	1/18	1/900	1/60	2/75

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[1] L. MINNHAGEN, Diss., Lund 1944, p. 28.

[2] L. MINNHAGEN, Ark. Fys., Bd 1, 1949.

[3] E. U. CONDON and G. H. SHORTLEY, Theory of Atomic Spectra, Cambridge 1935, p. 61—70, p. 245.

The factors $f(S\,L\,J)\cdot\frac{1}{4\,l^2-1}$ are tabulated by LOCHTE-HOLTGREVEN[1] and RYDE[2] for $\Delta L = \pm 1$; the analogous values for $\Delta L = 0$ are easily computed.

$({}^2P)$ $5\,p$ levels. From the energy level diagram of Si I (Fig. 2) it is evident that the $5\,p$ terms are perturbed by several other terms. We will discuss the $5\,p$ terms individually, assuming a field strength of 100 kV/cm.

$5\,p\ {}^3S_1$ lies more than 800 cm^{-1} from perturbing levels and the measured shift is only -0.7 cm^{-1}. An approximate calculation according to the above mentioned theory gives a shift of -1.5 cm^{-1}. The radial parts of the various Z^{α}_{β} are very probably smaller than those of hydrogen, used in this calculation. Furthermore, the main perturbing levels lie on the same side in relation to $5\,p\ {}^3S_1$. Hence this calculated shift of $5\,p\ {}^3S_1$ must be considered as an upper limit. These considerations apply in most of the following cases.

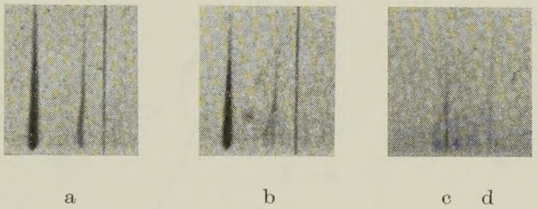

Fig. 1. Si I lines, a) λ 5948.6, $4\,s\ {}^1S_1 - 5\,p\ {}^1D_2$ at 120 kV/cm, b) ditto at 180 kV/cm (the almost unshifted "component" is the molecular hydrogen line λ 5949.9), c) λ 5772, $4\,s\ {}^1P_1 - 5\,p\ {}^1S_0$ at 89 kV/cm, d) λ 5701, $4\,s\ {}^3P_1 - 5\,p\ {}^3P_0$ at 89 kV/cm (the strongly shifted lines near c) and d) belong to F I).

The $5\,p\ {}^3P$ levels are perturbed by $4\,d\ {}^3P$, $5\,d\ {}^3D$ and $6\,s\ {}^3P$. An approximate calculation as indicated above gives shifts ranging from $+0.5$ to $+1.0$ cm^{-1} for all the M-states. The observations (Tab. 2), however, give no shift for the ${}^3P_0$ level and shifts of $+1.1$ cm^{-1} for ${}^3P_1$ and -1.3 cm^{-1} for ${}^3P_2$; these discrepancies are most probably due to the influence of the $4\,d$ ${}^3F_{2,3}$ levels, in spite of the fact that $\Delta L = 2$. The latter levels are situated close to and *between* the $5\,p\ {}^3P_{1,2}$ levels and are of course incapable of perturbing ${}^3P_0$. In Si I some weak lines from the combination $3\,p\ {}^3P - \mathrm{n}\,d\ {}^3F$ are classified by KIESS, proving that non-vanishing matrix elements Z^{α}_{β} connect states of these terms.

Of the $5\,p\ {}^3D$ levels only ${}^3D_3$ has been thoroughly studied. A calculation again shows that the perturbation must arise mainly from the $4\,d\ {}^3F$ levels but also, to a certain extent, from $6\,s\ {}^3P$, while the influence of other levels is negligible. The four M-states may be shifted at most $+3.5$ to $+5$ cm^{-1}; measurements of the unresolved ${}^3D_3$ level gives a shift of $+3$ cm^{-1}. The ${}^3D_2$ level is probably shifted by the same amount as ${}^3D_3$, but an accurate measurement of the shift of the line $4\,s\ {}^3P_1 - 5\,p\ {}^3D_2$, λ 5793.1, is prevented

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[1] W. LOCHTE-HOLTGREVEN, Z. Phys., *109*, 358, 1938.

[2] N. RYDE, Atoms and Molecules in Electric Fields, Lund 1942, p. 98 (in proof).

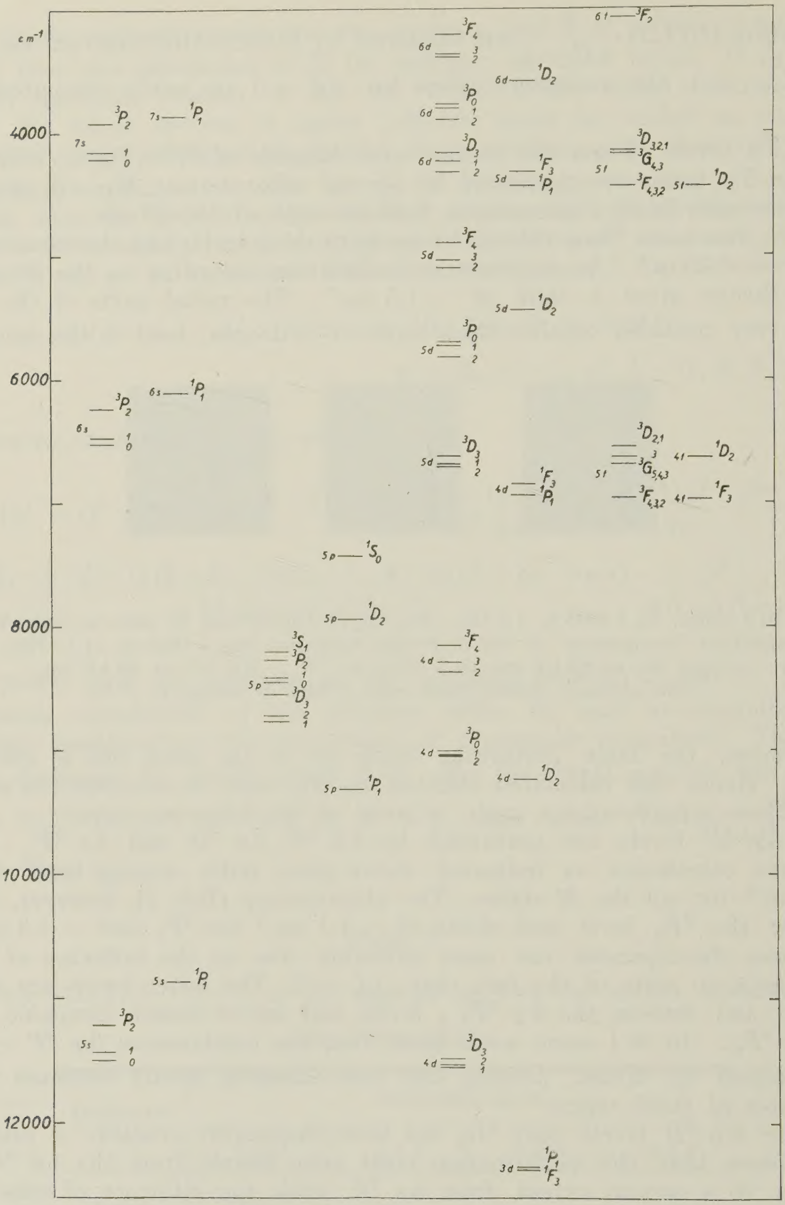

Fig. 2. Part of the energy level diagram of Si I.

by the nearby C I line, λ 5793.5. The observations on $^3D_1$ are uncertain, since the line $4s\ ^3P_0 - 5p\ ^3D_1$ is very faint.

$5p\ ^1S_0$ is the most shifted $5p$ level in spite of the fact that the distance to the main perturbing term, $4d\ ^1P_1$, is as large as 500 cm^{-1}. An approximate

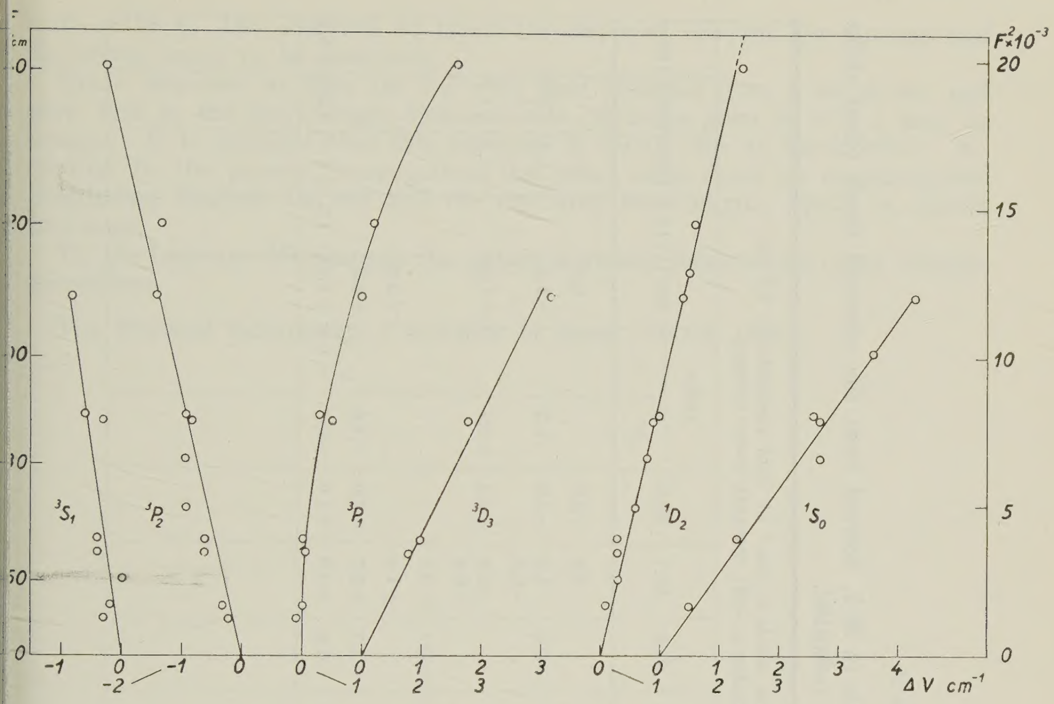

Fig. 3. Stark effect displacements of the Si I levels $(^2P)\ 5\,p\ ^3S_1,\ ^3P_1,\ ^3P_2,\ ^3D_3,\ ^1S_0,\ ^1D_2$.

calculation, however, gives a theoretical shift of + 4.5 cm^{-1} which compares well with the observed shift + 3.6 cm^{-1}.

Of all the Si I levels $5\,p\ ^1D_2$ has been most accurately investigated and has been observed at field strengths up to 180 kV/cm (Fig. 1). The perturbing terms are $4\,d\ ^1F_3$ and $6\,s\ ^1P_1$, while the influence from $4\,d\ ^1P_1$ must be negligible because of the small supermultiplet factor $f\,(L_{\rm I}\,l\,L)$. The calculation indicates that the σ-component of $4\,s\ ^1P_1 - 5\,p\ ^1D_2$ at 101 kV/cm (see Tab. 2) corresponds to the state $M = 2$ of $^1D_2$ (calculated shift + 0.5 cm^{-1}, observed + 0.9 cm^{-1}) and the π-component corresponds to $M = 1$ and 0 (calculated shift + 2.5 cm^{-1}, observed + 1.9 cm^{-1}). The polarized components were obtained experimentally by means of a Wollaston prism in front of the slit.

The Stark effect observed for the $5\,p$ levels is in most cases quadratic (Fig. 3).

$5\,f$ **levels.** As the $3\,d - 5\,f$ lines are weaker than the $4\,s - 5\,p$ lines, they have been observed only at relatively small field strengths (Tab. 2). The main perturbations certainly come from the unknown hydrogenic $5\,g$ terms and to a certain extent from the $6\,d$ terms. The field-free part of the line $3\,d\ ^3D_3 - 5\,f\ ^3G_4$, λ 6155.22, was observed on some spectrograms but at maximum field strength the line is strongly red-shifted and blends with the O I lines,

Table 2

Displacements of (^2P) $5p$ levels and some (^2P) $5f$ levels in Si I, derived from the observed Stark effect shifts of the lines indicated.

λ A	Undisplaced final level	Displaced initial level	Displacements of initial levels in cm^{-1} at field strengths in kV/cm: (+ sign indicates a shift towards lower energy)															
			35.5	41.1	50.6	58.7	62.6	70.4	81.3	88.7	89.9	101.0		109.7	113.5	120.4	140.6	180.4
												σ	π					
5684.52	$4s\,^3P_2$	$5p\,^3S_1$	−0.3	−0.2	0.0	−0.4	− 0.4			−0.3	−0.6			−0.8				
5708.44	$4s\,^3P_2$	$5p\,^3P_2$	−0.2	−0.4	−0.7m	−0.6	− 0.6	−0.9	−0.9	−1.0	−0.9	−1.3		−1.4		−1.3	−2.2	
5645.67	$4s\,^3P_1$	»	−0.2	−0.2		−0.2w				−0.6								
5690.47	$4s\,^3P_1$	$5p\,^3P_1$	−0.1	+0.1		+0.2	+ 0.1			+0.5	+0.3	+1.1		+1.0		+1.2	+2.6	
5665.60	$4s\,^3P_0$	»	−0.1	−0.1		−0.1	− 0.1			+0.4								
5701.14	$4s\,^3P_1$	$5p\,^3P_0$					− 0.4	−0.7(?)	+0.1	−0.1								
5797.91	$4s\,^3P_2$	$5p\,^3D_3$				+0.8	+ 1.0			+1.8				+3.2				
5772.26	$4s\,^1P_1$	$5p\,^1S_0$		+0.5			+ 1.3		+2.7	+2.7	+2.6	+3.6		+4.3				
5948.58	$4s\,^1S_1$	$5p\,^1D_2$		+0.1	+0.3	+0.3	+ 0.3	+0.6	+0.8	+0.9	+1.0	+0.9	+1.9	+1.4	+1.5	+1.6	+ 2.4	+5.2
6254.25	$3d\,^3D_3$	$5f\,^3F_4$		+0.9			+21.4											
6145.08	$3d\,^3D_2$	$5f\,^3G_3$	+2.8	+3.2			+11.2 + 4.2											
6243.86	$3d\,^3D_2$	$5f\,^3F_3$	+7.4	+ 9.9			+18.6											
6244.56	»	$5f\,^1D_2$	+3.1	+ 5.7														
				+2.4														

6155—6158 A. The observed $5f$ levels are displaced towards lower energy and the effect seems to be quadratic.

KIESS describes as hazy the $3d - 5f$ lines obtained from a silicon arc and says that in the wave-length measurements errors as great as 0.10 A may be present. It is probable that this hazyness is mainly due to Stark effect. According to the present investigation, this effect must cause an unsymmetrical broadening towards the red and the measured wave-lengths would be slightly too large.

To Dr. LENNART MINNHAGEN the author is greatly indebted for many valuable discussions.

The Physical Laboratory, University of Lund. March 1949.

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Errata

Page 215: the legend of Fig. 1 should read: . . . a) λ 5948.6, $4s\,{}^1P_1 - 5p\,{}^1D_2$ . . . c) λ 5708, $4s\,{}^3P_2 - 5p\,{}^3P_2$ . . .

» 216: in Fig. 2, the lowest *f*-levels: for $5f$, read $4f$.

» 217: line 5: for . . . $4d\,{}^1F_3$, read $4d\,{}^1F_3$, ${}^1D_2$.

» 218: table 2, λ 5948.58: for $4s\,{}^1S_1$, read $4s\,{}^1P_1$.